Microscopic calculations on Raman scattering from acoustic phonons confined in Si nanocrystals

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Raman scattering from the acoustic phonons confined in Si nanocrystals is investigated by a microscopic lattice dynamical calculation. Polarized and depolarized Raman spectra are found to be rather different, indicating from different acoustic phonons. The polarized scattering is more pronounced than the depolarized one. The calculated results are compared with the recent experimental data. The effects of matrix are discussed.

Recently, considerable attention has been paid to Si nanostructures since the discovery of the efficient photoluminescence from porous Si at room temperature.[1] Raman spectroscopy has been intensively used to characterize porous Si[2−4] and Si nanocrystals.[5,6] A phenomenological phonon-confinement model[7,8] has been widely used to quantitatively describe the Raman scattering from optical phonons. Very recently, microscopic calculations have been carried out to study the Raman spectra from the optical phonons confined in Si nanocrystals by the authors.[9,10]

As a matter of fact, when the sizes of nanocrystals decrease, phonons with large wave-vectors will be involved in the electron-phonon interaction. As a result, the scattering of electrons by acoustic phonons is expected to be more pronounced as compared to that by optical phonons. Experimentally, Raman scattering from confined acoustic phonons has been reported in glasses,[11] metals[12−14] and semiconductor nanocrystals.[15−18] More recently, Raman spectra from the acoustic phonons confined in Si nanocrystals dispersed in SiO₂ thin films have been reported.[19]

On the theoretical side, the confined acoustic phonons in nanocrystals have been studied by assuming a spherical elastic continuum based on the theory developed by Lamb[20,21] more than a century ago. The application of this theory to Si nanocrystals is, however, far from satisfactory.[19] The first reason may stem from the oversimplified assumption that the nanocrystal sphere is elastically isotropic, whereas Si is highly elastically asymmetric. The second is that the assumption of an elastic continuum may not be valid for nanocrystals with small size. The predicted Raman frequencies of the confined acoustic phonons in Si nanocrystals by using Lamb's theory are much higher than the experimental data.[19] As pointed out by Fujii *et al.*[19] that in this case lattice dynamical calculations are desired, which motivates us to develop a microscopic calculation.

Nanocrystals are normally dispersed in some matrices. The effects of surrounding matrix on the confined acoustic phonons have recently been studied by

several authors[18,21,22] using an elastic continuum theory. Contradictory conclusions were made. Ovsyuk and Novikov[18] claimed that the matrix effects are important, while Montagna and Dusi[22] reported that the influences of matrices are rather small and can be negligible. We try to clarify this problem by a lattice dynamical calculation from a microscopic point of view.

In the present work, we calculate the Raman spectra from the acoustic phonon confined in Si nanocrystals by a lattice dynamical calculation. The Si nanocrystals are assumed to have spherical shapes. In our lattice dynamical calculations, it is assumed that Si atoms are located at their diamond lattice sites and no relaxation exists as has been done in the previous work to study the optical phonons.[9,10] As a first approximation, the force constants in Si nanocrystals are taken to be the same as those in the bulk. A partial density approach is adopted to calculate the force constants in crystalline Si.[23,24] Force constants up to the fifth nearest neighbors are considered.

The spectral density of the scattered light is given by[25]

$$I_{\mu\nu}(\mathbf{q},\omega) \propto \int dt \exp(-i\omega t)\, \langle \delta\epsilon_{\mu\nu}^{*}(\mathbf{q},0)\delta\epsilon_{\mu\nu}(\mathbf{q},t) \rangle, \quad (1)$$

where μ and ν are the polarization direction of the incident and scattered photon; $\hbar\omega = \hbar\omega_i - \hbar\omega_s$ and $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ are the exchanged energy and wave-vector. The fluctuations of the dielectric constant can be described in terms of the space Fourier transformation of the macroscopic polarizability density tensor $P_{\mu\nu}(\mathbf{r},t)$

$$\delta\epsilon_{\mu\nu}(\mathbf{q},t) \propto \int d\mathbf{r} \exp[-i\mathbf{q}\cdot\mathbf{r}(t)]P_{\mu\nu}(\mathbf{r},t)$$
$$= \sum_i \exp[-i\mathbf{q}\cdot\mathbf{r}^i(t)]\alpha_{\mu\nu}^i(t). \quad (2)$$

Here $\alpha_{\mu\nu}^i(t)$ is the instantaneous polarizability of the ith scatter at the instantaneous position $\mathbf{r}^i(t) = \mathbf{R}^i + \mathbf{u}^i(t)$, where $\mathbf{R}^i$ is the equilibrium position of the ith scatter and $\mathbf{u}^i$ is the displacement from the equilibrium due to the phonon vibrations. Since we are interested in Raman

scattering from nanocrystals with size L small compared with the wavelength of the light ($qL \ll 1$), and not in the Brillouin scattering, we have $\mathbf{q} \sim 0$. The effective microscopic polarizability $\alpha_{\mu\nu}^i(t)$ can be expanded in terms of the displacements $\mathbf{u}^i$, and $\mathbf{u}^i$ can be expressed in terms of the vibrational eigenvectors $\mathbf{e}(i, p)$, the frequency of which is ω_p. The contribution of the pth phonon mode to the Stokes part of the Raman spectra is then given by[26]

$$I_{\mu\nu}(\omega_p) \propto \frac{n(\omega_p, T) + 1}{\omega_p} C_{\mu\nu}(\omega_p), \qquad (3)$$

where $n(\omega, T)$ is the Bose-Einstein population factor at temperature T and $C_{\mu\nu}(\omega_p)$ is the mode-radiation coupling coefficient given by

$$C_{\mu\nu}(\omega_p) = \left| \sum_{ij} \sum_{\gamma} \frac{\partial \alpha_{\mu\nu}^i}{\partial u_\gamma^j} [e_\gamma(j, p) - e_\gamma(i, p)] \right|^2. \qquad (4)$$

The quantities $A_{\mu\nu\gamma}^{ij} = \partial \alpha_{\mu\nu}^i / \partial u_\gamma^j$ depend on the scattering mechanism. A bond-polarizability (BP) model[27] is adopted in the present work to deal with the quantities $A_{\mu\nu\gamma}^{ij}$. The detailed description of the BP model can be found elsewhere.[28] Within the frame work of BP model, the polarizability of the whole system is calculated as a sum of independent contributions from every bond in the system based on the calculated eigenvalues and eigenvectors. The quantities $A_{\mu\nu\gamma}^{ij}$ are nonzero only if i and j are nearest atoms. The Raman intensity in the $\mu\nu$ polarization for backscattering configuration is finally given by

$$I_{\mu\nu}(\omega) \propto \sum_p \frac{n(\omega_p, T) + 1}{\omega_p} \delta(\omega - \omega_p) C_{\mu\nu}(\omega_p). \qquad (5)$$

Neither Frölich interactions nor electro-optic effects are incorporated. The polarized and depolarized Raman spectra I_p and I_d are obtained by averaging over the different directions of polarization

$$I_p = \frac{1}{3} \left(I_{xx} + I_{yy} + I_{zz} \right), \qquad (6)$$

$$I_d = \frac{1}{3} \left(I_{xy} + I_{yz} + I_{zx} \right). \qquad (7)$$

By using the force constants the dynamical matrix of a Si nanocrystal can be constructed. Eigenfrequencies and eigenvectors can be obtained by solving the secular equation about the dynamical matrix. Raman spectra are then calculated by the BP model based on the obtained eigenfrequencies and eigenvectors.

Figure 1 shows the calculated polarized and depolarized Raman spectra from the acoustic phonons confined in Si spheres without matrix. For a Si sphere the size is measured by its diameter, given by $L = (3N/4\pi)^{1/3}a$, where N and a are the number of Si atoms and the lattice constant of crystalline Si, respectively. Raman peaks

can be clearly seen in each spectrum. In the polarized spectrum, there is a Raman peak, labeled as peak 2. By inspecting the atomic displacements, LA-like phonons are found to be responsible for this peak. There is a small peak (peak 4) at the higher frequency, which originates from the higher-order LA-like confined phonons similar to the higher-order folded LA phonons in superlattices.[28] In depolarized spectrum, there is a Raman peak, labeled as peak 1. TA-like phonons are responsible for this peak. A rather small peak (peak 3) with the same frequency as the polarized peak 2 exists, which indicates that LA-like phonons also contribute to the depolarized scattering. As the size decreases, the peaks 1-4 shift to higher frequency. The intensity of the depolarized peak 1 is always smaller than that of the polarized peak 2. The intensity ratio of the two peaks in the depolarized and polarized scattering is roughly about 0.3 for all Si spheres studied here, which agrees fairly well with the experimental result of 0.25.[19] From Fig. 1, it can be seen that the peak positions depend strongly on the sizes of Si spheres.

In order to get the insight into the size dependencies, the peak frequencies as a function of the inverse size are given in Fig. 2. The bulk bands of sound waves, obtained by a simple correspondence between the wave-vector and size $q = \pi/L$, are also given as hatched areas for reference. This correspondence should be valid at least for very large size. For sound waves propagating in crystalline Si, only in some high-symmetrical directions are these waves purely longitudinal or transverse. In general, they have components of both. In an arbitrary direction quasi-longitudinal (QL) and quasi-transverse (QT) modes are obtained. The upper hatched area corresponds to the QL bands and the lower one to the QT bands.

The confined acoustic phonons in an isotropically elastic sphere were previously studied by Lamb's theory.[20,21] Two types of confined acoustic modes, spheroidal and torsional modes, were derived. The frequencies of these two modes were found to be proportional to the sound velocities in spheres and inversely proportional to the sphere size. The spheroidal and torsional modes are characterized by a quantum number l. From the selection rules, Raman-active modes are spheroidal modes with $l = 0$ and 2.[29] The $l = 0$ mode produces totally polarized spectra, while the $l = 2$ one partially depolarized spectra. This model has been used in many previous studies and could explain some experimental results. The results based on Lamb's theory are also given in Fig. 2 as dashed lines. The lines for every l stand for different propagating directions, since the sound velocity of Si is different for different propagating direction.

It can be seen from Fig. 2 that the results from Lamb's theory are systematically two times as larger as the experimental data. It should be noted that in experiment Si nanocrystals are surrounded by SiO_2 matrix. Even by taking the matrix effects into account, the results predicted by Lamb's theory are still much larger than the experimental ones.

The results obtained by the lattice dynamical calcula-

tion given in the figure are for Si nanocrystals without any matrix. The frequencies of the polarized peaks are outside the QL bands, which indicates that the effective sound velocity for LA-like phonons is lower than the bulk counterpart and is somewhat *softened* due to the finite size. The frequencies of the depolarized peaks are just inside the QT bands for Si nanocrystals without matrix. It seems that the polarized and depolarized peak frequencies scale almost linearly with the inverse of size in the size range studied, as is predicted by Lamb's theory. By a careful analysis, we find that this is, however, not the case owing to the fact that the Raman peak frequencies should gradually merge into the bulk bands with the increase in size.

We do not attempt to compare our calculated results directly with the experimental ones, since the calculated results are without matrix, while Si nanocrystals in experiment are surrounded with SiO_2 matrix. In principle, we can study Si nanocrystals with any matrix and compare directly with experiment. There are, however, some difficulties: there is little information on the structure of matrix, the size of matrix, and the situation about the interface between nanocrystals and matrices. Our calculated results of Si nanocrystals without matrix are larger than the experimental data. We will show below that this disagreement is caused by the matrix effects. It is expected that the results of the lattice dynamical calculation should agree better with the experimental data for Si nanocrystals with large size since the matrix effects should be less important for nanocrystals with large size as. This can be seen by a simple extrapolation of the data obtained by a lattice dynamical calculation in the direction towards the larger size.

As mentioned above, there are controversies about the effects of matrices. To clarify this problem, the effects of matrix are studied by introducing some shells of matrix atoms. We must simplified the problem since we have little about the matrix as mentioned above. The matrix atoms are assumed to be located still at the diamond lattice and the force constants of the matrix atoms are the same as in those of Si nanocrystals. The only difference is that the matrix atom has an *effective* mass M_x. The calculated results are shown in Fig. 3. Our calculations reveal that the frequencies of the polarized and depolarized Raman peaks are very sensitive to the matrix. The frequencies of both polarized and depolarized Raman peaks are found to shift to lower frequencies owing to the effects of matrix. The downward frequency shift due to the matrix can explain the discrepancy between our results without matrix and the experimental ones.

Other set of force constants between matrix atoms is also probed. The conclusion is basically the same. The difference is a different amount of frequency shift. The importance of the effects of matrix on acoustic phonons can be understood by that fact that the vibrational amplitudes of acoustic phonons are large at the boundary. For optical phonons, the vibrational amplitudes are very small at the boundary that the Raman frequencies should be slightly affected by the matrix.[10] This has been demonstrated by our calculations.

In summary, we have investigated the Raman scattering from acoustic phonons confined in Si nanocrystals by a lattice dynamical calculation. The polarized and depolarized low-frequency Raman peaks originate from the confined LA-like and TA-like acoustic phonons, respectively. The polarized scattering is more pronounced than the depolarized one. The effects of matrix are important and will lead to a downward frequency shift for both polarized and depolarized Raman peaks.

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FIG. 1. Calculated Raman spectrea from the acoustic phonons confined in Si spheres with different sizes at room temperature. The solid (dashed) lines stand for polarized (depolarized) Raman spectra.

FIG. 2. Raman peak frequencies from acoustic phonons confined in Si nanocrystals versus the inverse of size. The results obtained by the lattice dynamical calculation are given as empty (solid) circles for polarized (depolarized) scattering for nanocrystals without matrix. The hatched areas are the bulk bands. The experimental results, taken from Ref. 19, are also given as empty (solid) squares for polarized (depolarized) peaks, respectively. Dashed lines are results by Lamb's theory.

FIG. 3. Calculated Raman frequency shifts $\Delta\omega = \omega - \omega_0$ for a Si nanocrystal of 2.39 nm owing to a matrix with a width of 0.39 nm, where ω and ω_o are the frequecny with and without a matrix.
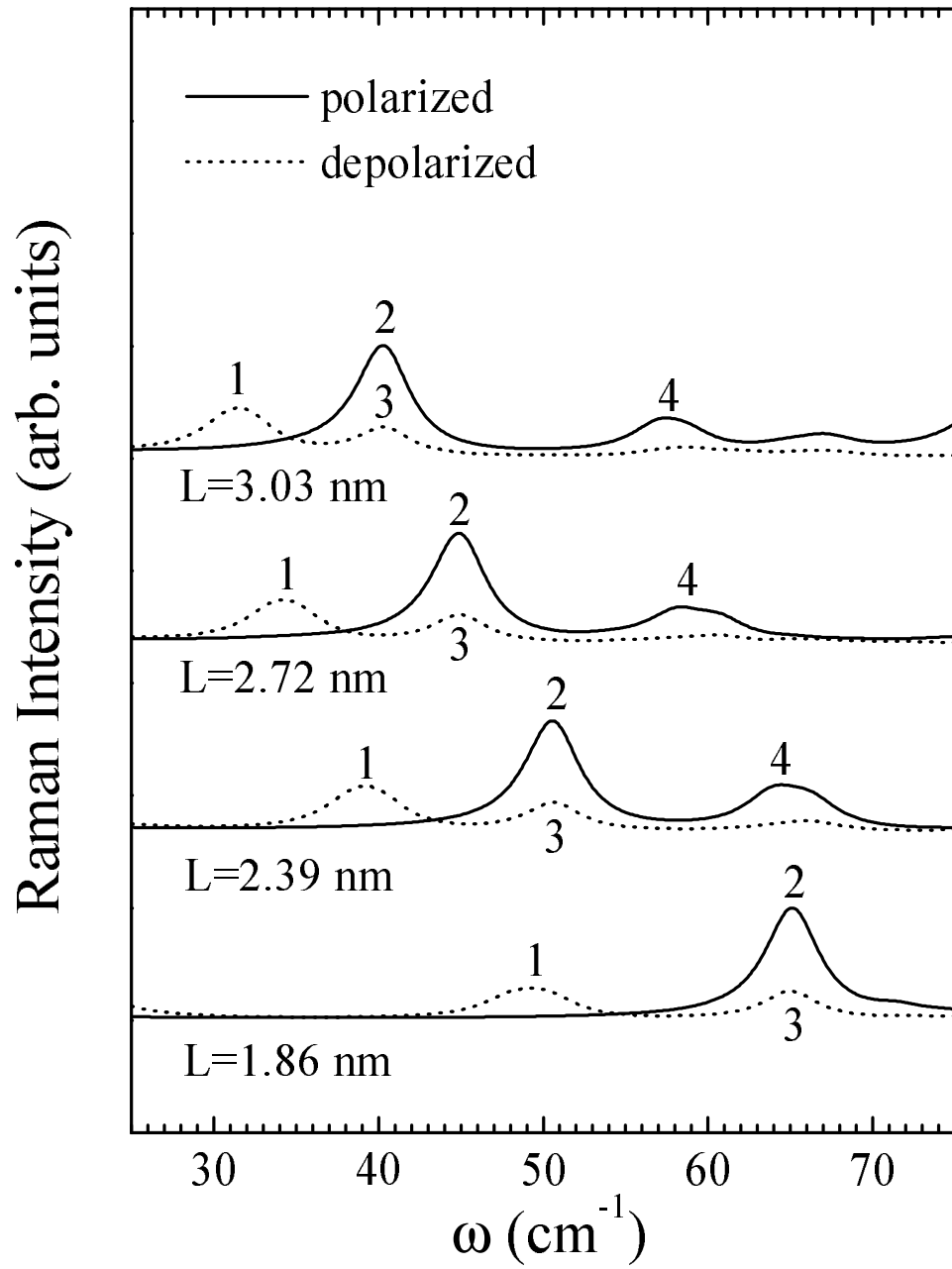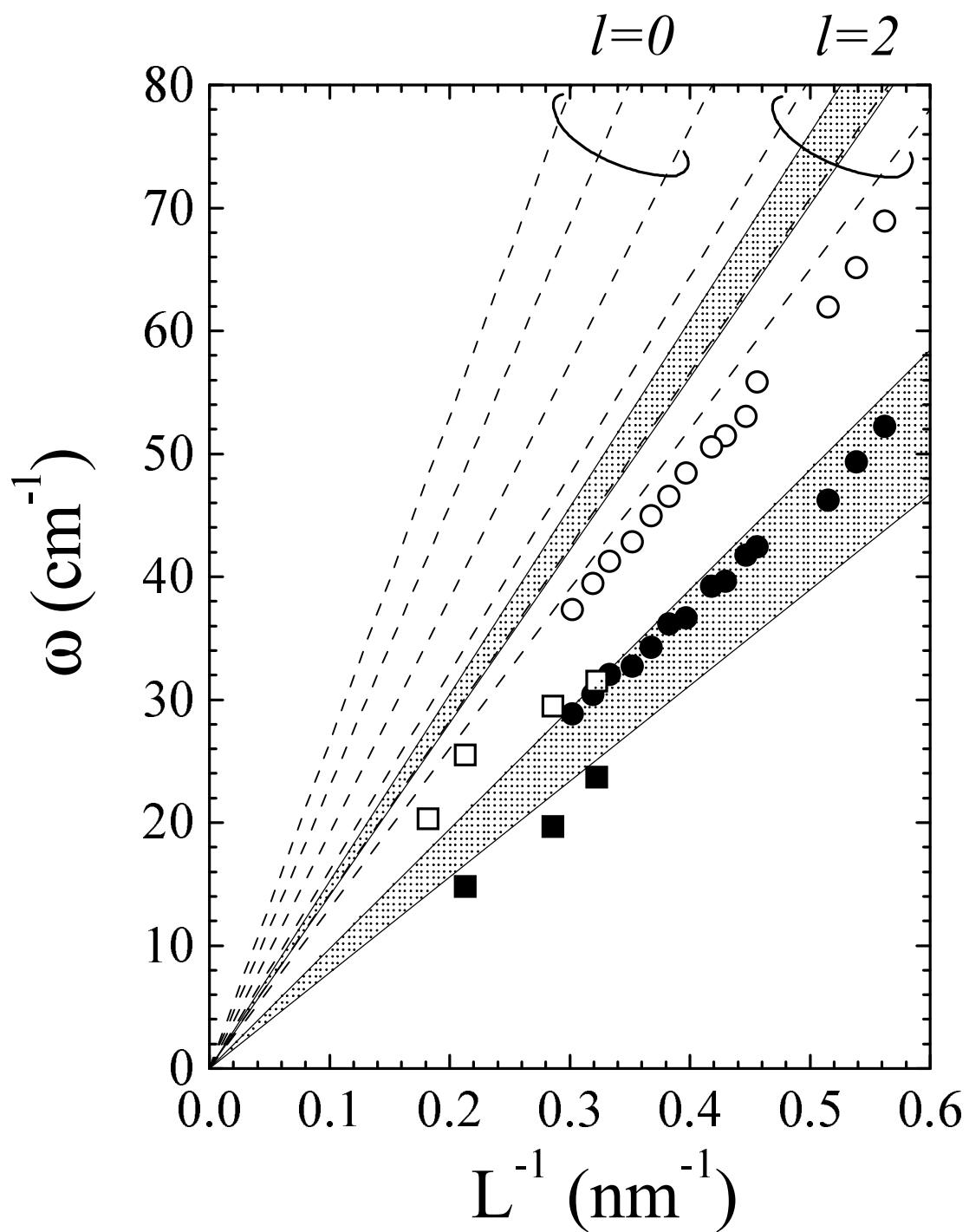
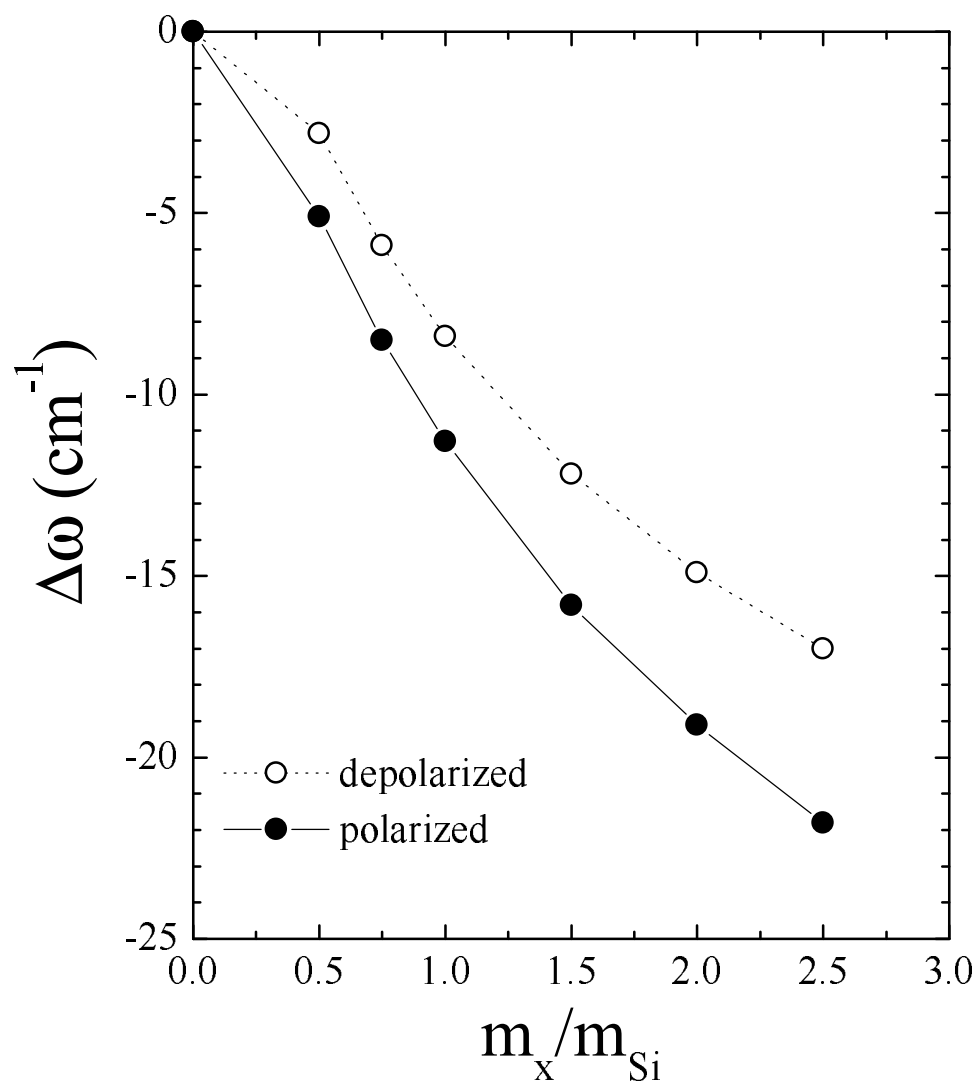Figure 1 J. Zi *et al.*

Figure 2 J. Zi *et al*.

Figure 3 J. Zi *et al.*